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PICOSECOND LASER STUDIES OF EXCITED STATE PROCESSES(U)
COLUMBIA UNIV NEW YORK DEPT OF CHEMISTRY K EISENTHAL
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FINAL REPORT OF RESEARCH ACCOMPLISHMENTS

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During the past three years of this contract we have made some excellent progress in our studies of key chemical and physical processes by which molecules in excited electronic states dissipate their excess energy. Many of these energy relaxing mechanisms and related molecular motions are so extremely rapid, especially in liquids, that they require special techniques for their study. To this end we have constructed sophisticated picosecond laser systems which enable us to detect transient absorption, emission and scattering events on the picosecond time scale. We have used these spectroscopic methods to address two important classes of chemical problems. One is the key role played by excited state intramolecular charge transfer processes in opening up new pathways for chemical change, energy transfer and decay in molecular systems. The second area is aimed at the key aspect of chemical reactions, namely the identification and study of the properties of the short-lived chemical intermediates occurring in chemical reactions.

I. Excited State Charge Transfer Phenomena

Photo-induced charge separation is one of the most important primary processes in photochemistry and photobiology. An excited molecule can dissipate its energy through charge transfer (CT) interaction with other ground state molecules, leading to the formation of an exciplex or an ion-pair. It can also redistribute the charges intramolecularly to form a large molecular dipole. We have studied the CT interaction in two prototype systems: (1) anthracene and dialkylaniline, and (2) p-cyanodimethylaniline. In the former system, either an exciplex or an ion-pair can be formed upon photoexcitation, while in the latter system a true intramolecular charge transfer occurs to form a large molecular dipole.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this research has been to increase our understanding of important chemical and physical pathways by which molecules in excited electronic states dissipate their energy. We have studied two broad classes of chemical problems. One is the key role of excited state charge transfer (CT) interactions in energy decay phenomena via the formation of an excited state charge transfer complex, an ion pair, or by the intramolecular redistribution of charge generating a very large molecular dipole. We have used picosecond transient absorp-		

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tion and emission techniques to study these processes in prototype systems: (a) excited anthracene + N,N¹-dimethylaniline, yielding exciplex and ion pair dynamics and (b) dimethylaminobenzonitrile (CH₃)₂-N-C₆H₅-C≡N (DMABN) representing the simplest case of a process now recognized to be common to a wide range of molecules, namely twisted internal charge transfer phenomena. From the studies on the anthracene system we obtained new information on molecular motions in liquids, on small chain dynamics using chromophores hooked together by a methylene chain, anthracene-(CH₂)₃-dimethylaniline, and new insights on the effects of geometry and solvent polarity on the dynamics of these processes. From this work we were able to develop ideas which explained a wide range of experimental findings appearing in the literature.

In our studies of twisted internal charge transfer in dimethylaminobenzonitrile, photo excitation of which leads to a twisting of the dimethylamino group perpendicular to the plane of the aromatic, we established that the stabilization of the twisted form is not only rapid in polar media but is in equilibrium with the initial, less polar excited form. We furthermore showed that for the case of alcohols as the solvent the stabilization is not only a long range dielectric polarization effect but also involves a short range complex between alcohol and the DMABN solute molecule.

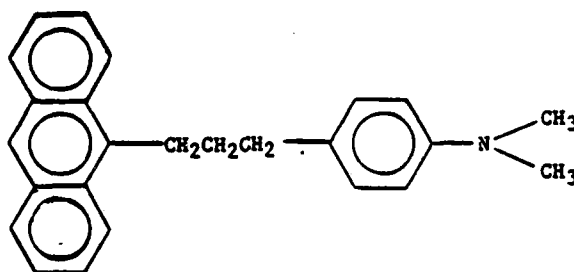
The second class of problems is concerned with the kinetics and properties of short-lived chemical intermediates generated by laser excitation of precursor molecules. Two systems which we have studied are the divalent carbon fragments (carbenes) R₁ - C - R₂, implicated in an enormous variety of chemical reactions and singlet oxygen, ¹O₂, a prime species in materials degradation.

The carbene that we have most extensively studied is diphenylcarbene, C₆H₅ - C - C₆H₅, which we generated by photodissociation of diphenyldiazomethane. We determined that the intersystem crossing time from the low lying singlet to the ground triplet state of diphenylcarbene took 90 ps in an alkane solvent. Combining this value with the measured triplet to singlet rate constant we obtained the equilibrium constant, free energy change and an estimate of the singlet-triplet energy gap. We extended our studies into a heretofore untouched area, namely excited state carbene chemistry. We proposed that the key point, in the reactivity of the excited triplet state of diphenylcarbene ³DPC, is the presence of an empty low lying orbital. Comparing the orbital diagrams of ³DPC, ¹DPC and ³DPC we noted that both ³DPC and ¹DPC have an empty low-lying orbital and suggested that the origin of the reactivity of ¹DPC and ³DPC was the same. We then carried out experiments which showed that ³DPC indeed reacts with alcohols in the same way as ¹DPC. From our studies of the reaction of ³DPC with amines we established the first example of a charge transfer interaction of carbenes with electron donors. The reaction mechanism is not the same as with the alcohols where reactivity is determined by acidity, but rather by a charge transfer mechanism.

In the singlet oxygen research we showed that one of the pathways in the photofragmentation of the endoperoxides of substituted anthracene, yielded not only an excited oxygen, ¹O₂, but also an electronically excited anthracene fragment. We established that though this route is conceptually important, i.e., generating two excited fragments, that the dominant decay pathway yielded the ground state (vibrationally hot) anthracene and ¹O₂. From our kinetics we also found evidence, previously unexpected, that a chemical intermediate of about 45 ps lifetime, is involved in the dissociation process. We are presently seeking to identify the intermediate.

A. Excited Charge Transfer Complexes.

Geometric Requirements. An important issue concerning the excited CT interaction is the role of the relative orientation between the donor and acceptor molecules. We approach this problem by connecting the anthracene and dimethylaniline (DMA) molecules with three methylene groups (I) to restrict their relative orientations while still maintaining their close proximity, maximum separation between them being less than 7 Å.



(I)

Upon excitation, this model molecule should form an intramolecular exciplex as rapidly as the anthracene and DMA system if there are no significant orientational requirements for CT interaction. On the other hand, if the time course for exciplex formation is different for the two cases, then molecular motions to achieve a favorable geometry must be involved and can be directly followed by monitoring the formation of the intramolecular exciplex.

We found in all the solvents studied that the formation of the intramolecular exciplex is slow, (on the nanosecond time scale) and strongly dependent on the solvent viscosity. As the viscosity increases, the formation

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rate decreases. If there were no geometric requirements for exciplex formation, then we know from our earlier results on the intermolecular exciplex that a rise time of 10 ps should be obtained. The much slower formation rate and the strong dependence on solvent viscosity which we find in the intramolecular case indicate that rotational motions are required to bring the two moieties into a favorable conformation to form the exciplex. The time dependence of this motion thus provides direct information about the end-to-end relaxation dynamics of this short chain molecule.

We also resolved a long standing debate on the role of intermediate structures from our observations that all the decay and formation curves can be fit with exponentials. The anthracene decay times and the exciplex formation times are found to be the same within experimental uncertainty in all the solvents studied. thus indicating that there is no long-lived non-fluorescent intermediate state present before the formation of the fluorescent exciplex.

The Effect of Solvent Polarity. The CT interactions, though determined by the intrinsic properties of the donor and acceptor pair, are greatly modified by environmental effects. Due to the charge separation associated with the CT interaction the solvent polarity can play an important role. To examine the interplay between geometric and solvent dielectric effects, we have studied A-(CH₂)₃-D in the strongly polar ($\epsilon = 37$) solvent acetonitrile.

In marked contrast to the results in nonpolar solvents, where the exciplex is formed in a few nanoseconds and lives for more than one hundred nanoseconds, we have found in acetonitrile that it is formed in a time shorter than we can resolve (< 2 ps) and decays in 580 ± 30 ps.

The very fast charge transfer rise suggests that only those molecules in a favorable ground state conformation at the time of excitation lead to the

exciplex. For those molecules in unfavorable extended conformations a new nonradiative decay channel is responsible for the observed 7 ps lifetime of the excited anthracene moiety. We believe this new ultrafast decay channel is direct e^- transfer to form a nonfluorescent ion-pair which is strongly stabilized by the polar solvent.

How then do geometrical restraints and solvent polarity as seen from these studies determine the dynamics and nature of the charge transfer process? For exciplexes in general, we proposed and supported with our data and data from the literature, that the geometric effects on formation rates are greatly affected by the energy separation between the locally excited singlet state and the exciplex state; the geometric constraints becoming less stringent as the energy increases. The solvent enters this process by stabilizing the polar exciplex state and thus changing the energy gap and thereby the driving force of the charge transfer process. Using this idea we were able to explain a wide range of experimental findings.

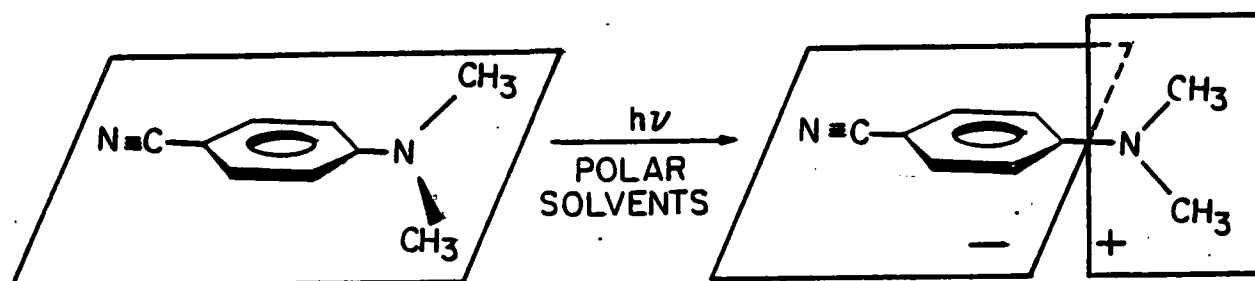
We also discovered in the course of this work that there are different ground state conformers in the three chain system which have different dynamics of exciplex formation. We obtained evidence for two different conformers whose structure possibly differs in the relative orientation of the anthracene and dimethylaniline chromophores. From our viscosity studies we concluded that it is the methylene chain motions which determine the viscosity dependence of the rates. The end groups alter the time of formation but the functional dependence on viscosity is determined by the methylene chain. We furthermore concluded that a single chain relaxation mode determines the rate of exciplex formation, perhaps the large scale end to end mode.

B. Twisted Internal Charge Transfer Phenomena.

Following photoexcitation of a molecule the intramolecular redistribution of charge can lead to a significant structure change and an associated large

change in dipole moment. Dimethylaminobenzonitrile is a prime example of this phenomena. In nonpolar solvents a single fluorescence band is observed. However in polar solvents an additional emission is observed in the visible which is associated with a large dipole moment, ~ 16 Debye. Both bond twisting and solvation are important in generating the new charge distribution.

We have been investigating this process which is now recognized to be of marked importance in a wide variety of molecular systems.



From our studies of the dynamics of the rise time of the polar, solvent stabilized form, and the decay times of both the "nonpolar", low dipole form and the polar form we established that the change in structure due to the twisted internal charge transfer was not only extremely fast but that the two forms were in equilibrium, a heretofore unknown result. To investigate the origin of the stabilization of the polar form in polar media we used polar nonpolar solvent mixtures of alcohols and alkanes and showed that the key step in the stabilization of the twisted intramolecular charge transfer structure is a short range interaction, namely the formation of a complex between excited DMABN and the alcohol. The twisted structure is further stabilized by interacting with the solvent dielectric as reflected by the continuing shift of the emission maximum to the red as the alcohol concentration is increased. We thus conclude that both specific short range interactions and

long range interactions are contributing to the stabilization of the twisted internal charge transfer state. Whether these results are applicable to other polar solvents and to other molecules undergoing excited state charge transfer twisting remains to be determined.

II. Short-Lived Chemical Intermediates.

A. Carbenes - Ground State and Excited State Properties.

Divalent carbon atom species, $R_1-\overset{''}{C}-R_2$, commonly referred to as carbenes, have widespread appeal to theoretical and experimental chemists. The main reason for the attention is that carbenes are proven to be important chemical intermediates which demonstrate a high reactivity toward a host of molecules. The two nonbonding electrons combine to give a singlet and triplet state; the triplet being the one of lower energy for most carbenes. The proximity of the low-lying singlet to the ground triplet state influences the photophysical and chemical properties of carbenes. Although the singlet and triplet states are at comparable energies, as for example in the case of diphenylcarbene, $C_6H_5-\overset{''}{C}-C_6H_5$, the chemistry of the two states is very different.

In our studies of diphenylcarbene, DPC, we have measured the very rapid spin interconversion from the singlet to the ground triplet state following photofragmentation of the precursor molecule, diphenyldiazomethane. Combining this result with the rate constant for the reverse process, measured by Professor N. Turro, we obtained the equilibrium constant for the two states, their free energy difference, and an estimate of the singlet-triplet energy gap, $\sim 1400\text{ cm}^{-1}$ in alkane solvents.

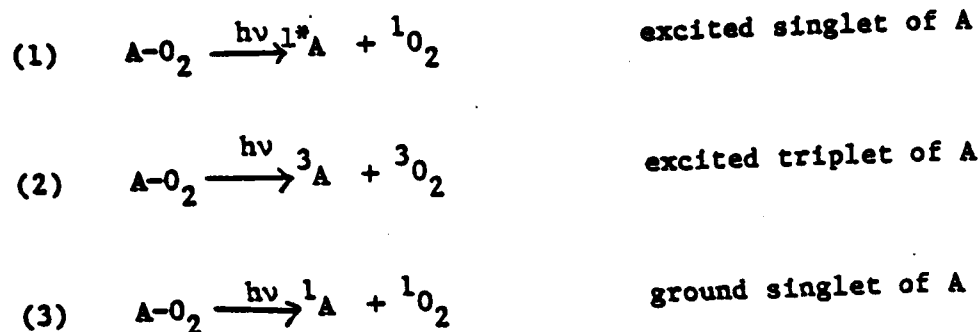
Although the chemistry of the low-lying states has been extensively studied, the chemistry in the higher states remain unknown in large part

due to the reactivity of the thermally accessible singlet and ground triplet states. In order to delineate the properties of the excited triplet state, 3^* DPC, and equally important, to establish its chemistry we initiated a study of this untouched area of excited state carbene chemistry. We proposed that the key point, in the reactivity of 3^* DPC is the presence of an empty low lying orbital. Comparing the orbital diagrams of 3^* DPC, 1 DPC and 3^* DPC we noted that the origin of the reactivity of 1 DPC and 3^* DPC was the same. We then carried out experiments which showed that 3^* DPC reacts with alcohols in the same way as 1 DPC, namely by attacking the OH bond rather than the CH bond of the alcohols. We showed that the reactivity with alcohols followed the acidity of the alcohol and was not related to the electron donating ability of the alcohol.

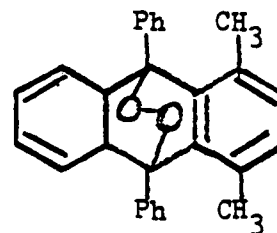
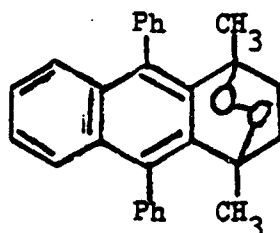
In our study of the reactions of 3^* DPC with amines and other molecules that have low ionization potentials we demonstrated that the reaction mechanism was a single electron charge transfer process. This is the first example of a charge transfer interaction of carbenes with electron donors. The reaction mechanism is not the same as with the alcohols where reactivity is determined by acidity, but rather by a charge transfer mechanism in the present case.

B. Singlet Oxygen.

In earlier work we showed that one of the pathways in the photofragmentation of the endoperoxides of substituted anthracenes, AO_2 , yielded an electronically excited anthracene fragment as well as the excited oxygen, $1O_2$. To determine the various photodissociative routes in addition to the one mentioned above, we considered the following spin allowed processes:



We studied the following two molecules:



Using triplet-triplet absorption to probe for the appearance of ${}^3A^*$, i.e. mechanism (2) we concluded that this process was not important. Using a laser induced fluorescence method we found that path (3) is the dominant one. However, we observed that the kinetics of formation of (3) differed from (1). This was an unexpected result pointing to the presence of a chemical intermediate that we are presently seeking to identify.

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